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SAIKI TAKEAKI(54) PRODUCTION OF SILYLATED POLYSULFIDE POLYMER, AND SILYLATED
POLYSULFIDE POLYMER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for easily synthesizing a silylated polysulfide polymer capable of not only being imparted a function for vulcanizing a rubber having a double bond by containing a recurrence of a number of sulfur bonds exceeding that of disulfide in its main chain, but also containing an alkosilyl group having a bond with silica by a hydrolysis in its terminal, and sometimes having a required chemical structure such as a benzothiazol group, thiocarbamyl group, etc., having a vulcanization accelerating effect, and to obtain a new silylated polysulfide polymer by the above method.

SOLUTION: This method for producing a silylated polysulfide polymer is to perform a sulfur interchanging reaction of a compound of the formula: $R_8S(R_1Sy)_nR_1SR_8$ and/or $R_8Sy(R_1Sy)_nR_1SyR_3$ with a compound of the formula: R_2SyR_2 to obtain a liquid compound at a normal temperature, expressed by the formula $R_2(SxR_1)_nSxR_2$. Provided that in the formulae, (x) represents a number exceeding 2 and up to 6, (y) represents a number of ≥ 2 , and (n) is 1-100 integer.

JAPANESE

[JP,2000-063521,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL
FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE

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CLAIMS

[Claim(s)]

[Claim 1] A compound expressed with general formula R^8S (R^1 Sy) nR^1SR^8 And/or, a compound expressed with R^8Sy (R^1 Sy) nR^1SyR^8 and a compound expressed with general formula R^2SyR^2 . A manufacturing method of a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^2(SxR^1) nSxR^2$ carrying out a sulfur exchange reaction. R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, And are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an

$R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and]
 An alkylene group of the carbon numbers 2-12 divalent [$^4 / R$] in an alkoxy group of the carbon numbers 1-8, and R^5 ,
 Or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group, or the ester, amide, and ether are expressed -- it is -- a case where R^2 is not the above-mentioned thing -- an alkyl group of the carbon numbers 1-20, its ester, a polyoxyalkylene group, benzyl, a hydroxyalkyl group of the carbon numbers 2-18, and a hydroxy polyoxy alkyl group. $R^6R^7N(CS)$ - (however, R^6 and R^7 -- a methyl group, an ethyl group, a butyl group, and one alkyl group of the C_5H_{10} .) A thio carbamyl group which shows structure of benzyl, a xanthogenic acid group in which structure of $_2(CH_3)$ (CS) CHO- is shown, A benzothiazole group in which structure of C_6H_4SNC - is shown, And it is a basis chosen from a morpholine group in which structure of OC_4H_8N - is shown, R^2 which the same R^2 in R^2SxR^2 may be sufficient as, and is different may be sufficient as R^8 , x shows a value to 6 exceeding 2, and y shows two or more numerical values, and n is an integer which shows 1-100.
 [Claim 2] A compound expressed with general formula $R^8S(R^1 Sy) nR^1SR^8$ and/or $R^8S(R^1 Sy) nR^1SR^8$, and a compound expressed with general formula R^2SyR^2 . A manufacturing method of a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^2(SxR^1) nSxR^2$ carrying out a sulfur exchange reaction under existence of sulfur. R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, Are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4 / R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , Or an alkylene group of

the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group, or the ester, amide, and ether are expressed -- it is -- a case where R^2 is not the above-mentioned thing -- an alkyl group of the carbon numbers 1-20, its ester, a polyoxyalkylene group, benzyl, a hydroxyalkyl group of the carbon numbers 2-18, and a hydroxy polyoxy alkyl group. $R^6R^7N(CS)-$ (however, R^6 and R^7 -- a methyl group, an ethyl group, a butyl group, and one alkyl group of the C_5H_{10} .) A thio carbamyl group which

shows structure of benzyl, a xanthogenic acid group in which structure of $_2(CH_3)(CS)CHO-$ is shown, A

benzothiazole group in which structure of C_6H_4SNC- is

shown, And it is the basis chosen from a morpholine group in which structure of OC_4H_8N- is shown, R^2 which the

same R^2 in R^2SyR^2 may be sufficient as, and is different may be sufficient as R^8 , x shows a value to 6 exceeding 2, and y shows a numerical value exceeding 1, and n is an integer which shows 1-100.

[Claim 3] A compound expressed with general formula $HS(R^1Sy)nR^1SH$, A manufacturing method of a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^2(SxR^1)nSxR^2$ carrying out the sulfur exchange reaction of a compound expressed with general formula R^2SyR^2 , and the sulfur, and carrying out a polymerization reaction. R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, Are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4/R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , Or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group, or the ester, amide, and ether are expressed -- it is -- a case where R^2 is not the above-mentioned thing -- an alkyl group of the carbon numbers 1-20, its ester, a polyoxyalkylene group, benzyl, a hydroxyalkyl group of the carbon numbers

2-18, and a hydroxy polyoxy alkyl group. $R^6R^7N(CS)-$ (however, R^6 and R^7 -- a methyl group, an ethyl group, a butyl group, and one alkyl group of the C_5H_{10} .) A thio carbamyl group which shows structure of benzyl, a xanthogenic acid group in which structure of $_2(CH_3)$ (CS) $CHO-$ is shown, A benzothiazole group in which structure of C_6H_4SNC- is shown, And it is a basis chosen from a morpholine group in which structure of OC_4H_8N- is shown, R^2 which the same R^2 in R^2SxR^2 may be sufficient as, and is different may be sufficient as R^9 , x shows a value to 6 exceeding 2, and y shows a numerical value exceeding 1, and n is an integer which shows 1-100.

[Claim 4] A compound expressed with general formula $HS(R^1 Sy) nR^1 SH$, A manufacturing method of a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^2(SxR^1) nSxR^2$ carrying out the sulfur exchange reaction of a compound expressed with general formula $R^2 SH$, and the sulfur, and carrying out a polymerization reaction. R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, Are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4 / R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , Or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group, or the ester, amide, and ether are expressed -- it is -- a case where R^2 is not the above-mentioned thing -- an alkyl group of the carbon numbers 1-20, its ester, a polyoxyalkylene group, benzyl, a hydroxyalkyl group of the carbon numbers 2-18, and a hydroxy polyoxy alkyl group. $R^6R^7N(CS)-$ (however, R^6 and R^7 -- a methyl group, an ethyl group, a butyl group, and one alkyl group of the C_5H_{10} .) A thio carbamyl group which shows structure of benzyl, a xanthogenic acid group in which structure of $_2(CH_3)$ (CS)

CHO- is shown, It is a basis chosen from a benzothiazole group in which structure of C_6H_4SNC- is shown, and a morpholine group in which structure of OC_4H_8N- is shown, and x shows a value to 6 exceeding 2, and y shows a numerical value exceeding 1, and n is an integer which shows 1-100.

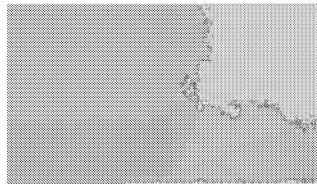
[Claim 5] General formula C_6H_4SNC . (SxR^1) A silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with $nSxR^2$, general formula $R^6R^7N(CS)$ (SxR^1) $nSxR^2$, or $OC_4H_8N(SxR^1)nSxR^2$. R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, Are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4/R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group or its ester, amide, and ether are expressed -- it is -- x shows a value to 6 exceeding 2, and n shows an integer of 1-100.

[Claim 6] General formula C_6H_4SNC . (SxR^1) $nSxR^2$. Or a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^6R^7N(CS)$ (SxR^1) $nSxR^2$ or general formula $OC_4H_8N(SxR^1)nSxR^2$. However, in the above-mentioned general formula, At least $R^1CH_2CH_2OCH_2OCH_2CH_2$,

$CH_2CH_2OCH_2CH_2OCH_2CH_2$, or $CH_2CH(OH)CH_2$. One or more are included and at least one R^2 in a general formula R^2 , An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4/R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , or an alkylene group of the divalent carbon numbers 2-12 which has the ester,

amide, ether, or a hydroxyl group or its ester, amide, and ether are expressed -- it is -- x shows a value to 6 exceeding 2, and n shows an integer of 1-100.

[Translation done.]



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[JP,2000-063521,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of a silanizing polysulfide polymer and the new silanizing polysulfide polymer which are fluids at the ordinary temperature whose average bonding number of sulfur of a repeating unit is six or less exceeding 2. This invention relates to the manufacturing method of a suitable silanizing polysulfide polymer and the new silanizing polysulfide polymer used as silica and the binding material of the polymer which has a double bond.

[0002]

[Description of the Prior Art]Using silicate as a reinforcing agent of the rubber which has a double bond has spread widely in the field of industry. If the silica which is

hydrophilic nature is blended with the rubber which is hydrophobicity, familiarity in rubber and silica will be bad and various problems will be derived. The bis(3-triethoxy silyl propyl)tetrasulfide which serves as rubber and a binding material of silica as one of the solution of this is used. However, since the molecular weight is low, it is difficult for this thing for rubber and silica to join together uniformly. It is convenient for distribution to become uniform and for the contacting efficiency of silica and rubber become high if a molecular weight is made high. JP,9-3248,A responds to this request and to this. How to compound a silanizing polysulfide polymer with a non-aqueous solvent from an mercaptosilane, JICHIORU, and sulfur dichloride, And the method of compounding a silanizing polysulfide polymer under a non-aqueous solvent is described in silanizing alkyl halide, dihalogen-ized alkyl, and metal polysulfide. However, since the viscosity of that it is necessary to make it react by perfect non-watery voice, needing a lot of solvents, and output became high, these methods had problems, like separation with the halogenation metal which carries out a byproduction is difficult. The silanizing polysulfide compound with a thio carbamyl group which is a low molecular weight compound is indicated by JP,6-25284,B, It is indicated that this compound has the feature of reducing Mooney viscosity (workability) in the system which used silica for the rubber which has a double bond as a reinforcing agent rather than the increase of disruptive strength and bis(3-triethoxy silyl propyl) tetrasulfide. However, since this compound had the low molecular weight, it needed to use in large quantities, and when small, an effect was not enough and was a problem. [0003]

[Problem(s) to be Solved by the Invention]It not only gives the function as a **** agent of rubber which has a double bond by including a repetition of the bonding number of the sulfur which the purpose of this invention cancels the above-mentioned conventional fault, and exceeds disulfide to a main chain, but, An end certainly contains the Al Kosi Lil group which has unity with silica by hydrolysis, It is in providing the new silanizing polysulfide polymer which is acquired by the method of compounding easily, and a method for the same, and deals in the silanizing polysulfide polymer which has the chemical structure demanded [which

have a vulcanization facilitatory effect of rubber depending on the case / a benzothiazole group, a thio carbamyl group, etc.].

[0004]

[Means for Solving the Problem] A technical problem of this invention was industrially attained conveniently by following this invention as a result of this invention persons' wholeheartedly examination.

[0005][1] General formula R^8S . (R^1 Sy) A compound expressed with compound and/or general formula $R^8Sy(R^1$ Sy) nR^1SyR^8 expressed with nR^1SR^8 , and a compound expressed with general formula R^2SyR^2 . A manufacturing method of a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^2(SxR^1) nSxR^2$ carrying out a sulfur exchange reaction.

[0006] R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, Are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4 / R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , Or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group, Or the ester, amide, and ether are expressed. Are, and when R^2 is not the above-mentioned thing, an alkyl group of the carbon numbers 1-20, its ester, a polyoxyalkylene group, benzyl, a hydroxyalkyl group of the carbon numbers 2-18, a hydroxy polyoxy alkyl group, $R^6R^7N(CS)-$ (however, R^6 and R^7 -- a methyl group, an ethyl group, a butyl group, and one alkyl group of the C_5H_{10} .) A thio carbamyl group which shows structure of benzyl, a xanthogenic acid group in which structure of $_2(CH_3) (CS) CHO-$ is shown, A benzothiazole group in which structure of C_6H_4SNC- is shown, And it is a basis chosen from a morpholine group in which structure of OC_4H_8N- is shown, R^2 which the same R^2 in R^2SxR^2 may be sufficient as, and is different may be sufficient as R^8 , x

shows a value to 6 exceeding 2, and y shows two or more numerical values, and n is an integer which shows 1-100.
 [0007][2] A compound expressed with general formula $R^8S(R^1 Sy) nR^1SR^8$ and/or $R^8S(R^1 Sy) nR^1SR^8$, and a compound expressed with general formula R^2SyR^2 . A manufacturing method of a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^2(SxR^1) nSxR^2$ carrying out a sulfur exchange reaction under existence of sulfur.

[0008] R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, Are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4/R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , Or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group, or the ester, amide, and ether are expressed -- it is -- a case where R^2 is not the above-mentioned thing -- an alkyl group of the carbon numbers 1-20, its ester, a polyoxyalkylene group, benzyl, a hydroxyalkyl group of the carbon numbers 2-18, and a hydroxy polyoxy alkyl group. $R^6R^7N(CS)-$ (however, R^6 and R^7 -- a methyl group, an ethyl group, a butyl group, and one alkyl group of the C_5H_{10} .) A thio carbamyl group which

shows structure of benzyl, a xanthogenic acid group in which structure of $_2(CH_3)(CS)CHO-$ is shown, A benzothiazole group in which structure of C_6H_4SNC- is shown, And it is the basis chosen from a morpholine group in which structure of OC_4H_8N- is shown, R^2 which the same R^2 in R^2SyR^2 may be sufficient as, and is different may be sufficient as R^8 , x shows a value to 6 exceeding 2, and y shows a numerical value exceeding 1, and n is an integer which shows 1-100.

[0009][3] A compound expressed with general formula $HS(R^1 Sy) nR^1 SH$, A manufacturing method of a silanizing

polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^2(SxR^1)_nSxR^2$ carrying out the sulfur exchange reaction of a compound expressed with general formula R^2SyR^2 , and the sulfur, and carrying out a polymerization reaction.

[0010] R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, Are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4 / R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , Or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group, or the ester, amide, and ether are expressed -- it is -- a case where R^2 is not the above-mentioned thing -- an alkyl group of the carbon numbers 1-20, its ester, a polyoxyalkylene group, benzyl, a hydroxyalkyl group of the carbon numbers 2-18, and a hydroxy polyoxy alkyl group. $R^6R^7N(CS)-$ (however, R^6 and R^7 -- a methyl group, an ethyl group, a butyl group, and one alkyl group of the C_5H_{10} .) A thio carbamyl group which

shows structure of benzyl, a xanthogenic acid group in which structure of $_2(CH_3)(CS)CHO-$ is shown, A benzothiazole group in which structure of C_6H_4SNC- is shown, And it is a basis chosen from a morpholine group in which structure of OC_4H_8N- is shown, R^2 which the same R^2 in R^2SxR^2 may be sufficient as, and is different may be sufficient as R^9 , x shows a value to 6 exceeding 2, and y shows a numerical value exceeding 1, and n is an integer which shows 1-100.

[0011][4] A compound expressed with general formula $HS(R^1Sy)_nR^1SH$, A manufacturing method of a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^2(SxR^1)_nSxR^2$ carrying out the sulfur exchange reaction of a compound expressed with general formula R^2SH , and the sulfur, and carrying out

a polymerization reaction.

[0012] R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, Are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4 / R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , Or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group, or the ester, amide, and ether are expressed -- it is -- a case where R^2 is not the above-mentioned thing -- an alkyl group of the carbon numbers 1-20, its ester, a polyoxyalkylene group, benzyl, a hydroxyalkyl group of the carbon numbers 2-18, and a hydroxy polyoxy alkyl group. $R^6R^7N(CS)-$ (however, R^6 and R^7 -- a methyl group, an ethyl group, a butyl group, and one alkyl group of the C_5H_{10} .) A thio carbamyl group which shows structure of benzyl, a xanthogenic acid group in which structure of $_2(CH_3)(CS)CHO-$ is shown, It is a basis chosen from a benzothiazole group in which structure of C_6H_4SNC- is shown, and a morpholine group in which structure of OC_4H_8N- is shown, and x shows a value to 6 exceeding 2, and y shows a numerical value exceeding 1, and n is an integer which shows 1-100.

[0013][5] General formula C_6H_4SNC . $(SxR^1)nSxR^2$. Or a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^6R^7N(CS)(SxR^1)nSxR^2$ or general formula $OC_4H_8N(SxR^1)nSxR^2$.

[0014] R^1 in the above-mentioned general formula However, an alkylene group of the carbon numbers 2-10, An oxyalkylene group of the carbon numbers 2-10 and the number of oxygen A polyoxyalkylene group of 2-20, Are at least one basis chosen from a hydroxy alkylene group of the carbon numbers 3-12, and R^2 , At least one R^2 in a general formula, An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the

carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4/R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group or its ester, amide, and ether are expressed -- it is -- x shows a value to 6 exceeding 2, and n shows an integer of 1-100.

[0015][6] General formula $C_6H_4SNC.(SxR^1)nSxR^2$. Or a silanizing polysulfide polymer which is a fluid at ordinary temperature expressed with general formula $R^6R^7N(CS)(SxR^1)nSxR^2$ or general formula $OC_4H_8N(SxR^1)nSxR^2$.

[0016]However, in the above-mentioned general formula, At least $R^1CH_2CH_2OCH_2OCH_2CH_2$,

$CH_2CH_2OCH_2CH_2OCH_2CH_2$, or $CH_2CH(OH)CH_2$. One

or more are included and at least one R^2 in a general formula R^2 , An $R^3R^3R^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 an alkyl group of the carbon numbers 1-4) [express and] An alkylene group of the carbon numbers 2-12 divalent [$^4/R$] in an alkoxy group of the carbon numbers 1-8, and R^5 , or an alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group or its ester, amide, and ether are expressed -- it is -- x shows a value to 6 exceeding 2, and n shows an integer of 1-100.

[0017]

[Embodiment of the Invention]This invention relates to the new silanizing polysulfide polymer which the average bonding number of sulfur of a repeating unit can acquire at the ordinary temperature which is six or less exceeding 2 with a manufacturing method of the silanizing polysulfide polymer which is a fluid, and a manufacturing method for the same.

[0018]The compound expressed with general formula $R^8S(R^1Sy)nR^1SR^8$ used in this invention can be obtained from the compound expressed with general formula $HS(R^1Sy)nR^1SH$. This $HS(R^1Sy)nR^1SH$ is U.S. Pat. No. 2466963 of Patrick and others, and JP,4-363325,A. It is chosen out of the compound etc. which were indicated. The sulphuric bonding number y of this polysulfide polymer is usually 2.

[0019]The compound expressed with general formula R^8S

(R^1 Sy) nR^1SR^8 by adding oxygen atom content cyclic ether compounds, such as ethyleneoxide or propylene oxide, to the compound expressed with general formula $HS(R^1$ Sy) nR^1 SH. It is obtained easily. It is easily obtained also by making it react to unsaturation groups, such as 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate. An end group is obtained also by carrying out the addition reaction of glycidylethers, for example, allyl, butyl, phenyl, methyl, 2-ethylhexyl, the stearyl group glycidyl ether, etc. to the polysulfide polymer which has a sulfhydryl group. It is obtained also by making the end SH of a polysulfide polymer react to aldehyde or ketone under an amine catalyst as indicated in the JP,41-19514,B gazette.

[0020]The isocyanatesilane to which $R^8S(R^1$ Sy) nR^1SR^8 whose end group is a silyl group has a silyl group in the polysulfide polymer whose end group is a sulfhydryl group or an OH radical, It is easily obtained by carrying out addition reactions, such as epoxysilane and vinylsilane. That in which x exceeds 2 is obtained by adding bottom sulfur of an amine catalyst to the polysulfide polymer produced by performing these addition reactions.

[0021]Compound expressed with general formula R^2SyR^2 used in this invention If it carries out, Dimethyl disulfide, diphenyl disulfide, JI t-dodecyl polysulfide, JI t-nonyl polysulfide, JI t-butyl disulfide, bis(3-trimethoxysilylpropyl) polysulfide, Bis(3-triethoxy silyl propyl)polysulfide, bis(3-trimethoxysilyl tolylene)polysulfide, Bis(3-triethoxy silyl tolylene)polysulfide, tetramethyl thiuram disulfide, Tetraethylthiuram disulfide, tetrabutylthiuram disulfide, Dipentamethylene CHIURAMUTETORA sulfide, dibenzothiazyl disulfide, 2-(4'-morpholine NOJICHIO) benzothiazole, dithio dimorpholine, SHISOPUROPIRU KISANTOGEN disulfide, tetrakis (2-ethylhexyl) thiuram disulfide, o, and o' dibenzamide diphenyl disulfide etc. are mentioned.

[0022]As a compound expressed with general formula R^2 SH, mercaptans, such as mercaptosilanes, such as gamma-mercapto propyltrimethoxysilane and gamma-mercaptopropyl triethoxysilane, and 2-mercaptobenzothiazole, are mentioned.

[0023]How to manufacture from $R^8S(R^1$ Sy) nR^1SR^8 and R^2SyR^2 in this invention, although polysulfide polymer $R^2Sx(R^1$ Sx) nR^2 is obtained, How to manufacture from R^8S

(R¹ Sy) nR¹SR⁸, R²SyR², and sulfur, There is the method of manufacturing from the method of manufacturing from HS (R¹ Sy) nR¹ SH, R²SyR², and sulfur, HS(R¹ Sy) nR¹ SH and R² SH, and sulfur. In this any case, an alkali catalyst is executable on the conditions of 30 hours 0 to 10% of the weight from 150 ** from the reaction temperature of 20 **, and reaction-time 5 minutes. When using an alkali catalyst, an amine catalyst, especially triethylamine have a large catalytic effect, and are [that a post process is comparatively easy to remove by that of low-boiling *****] convenient. 3 % of the weight of a catalyst amount is [reaction temperature / 30 ** to 100 **, and reaction time] more preferred from 0.01 % of the weight from 10 minutes for 5 hours. R²SyR² and/or R² SH to add receive raw material polysulfide polymer R⁸S(R¹ Sy) nR¹SR⁸ and/ or HS(R¹ Sy) nR¹SH100 weight section. Two to 500 weight section is preferably desirable one to 1000 weight section. The sulfur to add is stoichiometrically decided by the target x of purpose polysulfide polymer R²Sx(R¹ Sx) nR². [0024]In polysulfide polymer R²(SxR¹) nSxR² obtained with this manufacturing method. R² is an R³R³R⁴SiR⁵ group, an R³R⁴R⁴SiR⁵ group, or an R⁴R⁴R⁴SiR⁵ group (however, R³ the alkyl group of the carbon numbers 1-4). [express and] The alkylene group of the carbon numbers 2-12 divalent [⁴ / R] in the alkoxy group of the carbon numbers 1-8, and R⁵, or the alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group or its ester, amide, and ether are expressed. a case -- a double bond -- having -- rubber -- silicate -- a system -- a bulking agent -- it can set -- a binder -- ***** -- it can use .

[0025]When the silanizing polysulfide polymer obtained with this manufacturing method manufactures rubber or thermoplastic elastomer, it can not only be expectable as rubber's own vulcanizing agent, but can expect to raise the adhesive property of glass, rubber and glass, and thermoplastic elastomer by blending.

[0026]It is also possible to use as a vulcanizing agent of the rubber which has a double bond, and since it is a polymers vulcanizing agent, the heat resistance and stress relaxation which are not that of bloom can expect stabilization of the quality by the uniform dispersion of the vulcanizing agent to

rubber, rubber/rubber, rubber / resin, and improvement in quality well.

[0027]As rubber which it has, here a double bond Crude rubber, butadiene rubber, A styrene butadiene rubber, polyisoprene rubber, butadiene-acrylonitrile rubber, and its hydrogenation rubber, Isobutylene isoprene rubber, the halogenated isobutylene isoprene rubber, epichlorohydrin rubber, an ethylene-propylene-copolymer, an ethylene acetic acid vinyl copolymer, carboxy rubber, epoxide rubber, chloroprene rubber, acrylic rubber, millable urethane rubber, etc. are mentioned. It can use also not only to the independent system of these rubbers but to a blend system. It does not bar using it also for the rubber which has a double bond for dynamic bridge formation used as a thermoplastic elastomer. These uses Each part articles of a tire, such as a car, a bicycle, a track, a bus, and a motor bicycle, The material of various belts, various rollers, and shoes, various hose, a sheet, packing, a sound deadener, a base isolation material, a golf ball, wire insulation, covering material, a buffer element, a cable, a gasket, the parts for household appliances, the inner exterior face material for civil engineering and construction, etc. are mentioned.

[0028]In polysulfide polymer $R^2(SxR^1)nSxR^2$ obtained with this manufacturing method, $R^2 -- R^6R^7N(CS)-$ (however, R^6 and $R^7 --$ a methyl group, an ethyl group, a butyl group, and one alkyl group of the C_5H_{10} .) The thio carbamyl group which shows the structure of benzyl, the xanthogenic acid group in which the structure of $2(CH_3)$ (CS) CHO- is shown, In the case of the benzothiazole group in which the structure of C_6H_4SNC- is shown, and the morpholine group in which the structure of OC_4H_8N- is shown, since it can have not only the effect as a vulcanizing agent of rubber of having a double bond but an effect of a rubber accelerator, it is more advantageous. The heat resistance and stress relaxation nature which are not that of bloom can expect stabilization of the quality by the uniform dispersion of the vulcanizing agent to rubber, rubber/rubber, rubber / resin, and improvement in quality well.

[0029]Although indicated to claims 5 and 6 of the claim of this application, an end -- $R^6R^7N(CS)-$ (however, R^6 and $R^7 --$ a methyl group, an ethyl group, a butyl group, and one

alkyl group of the C_5H_{10} .) Benzyl. Or C_6H_4SNC- . Or OC_4H_8N- . An R^3R^3R [not only having but] $^4SiR^5$ group, an $R^3R^4R^4SiR^5$ group, or an $R^4R^4R^4SiR^5$ group (however, R^3 the alkyl group of the carbon numbers 1-4) [express and] The alkylene group of the carbon numbers 2-12 divalent [4R] in the alkoxy group of the carbon numbers 1-8, and R^5 , Or the alkylene group of the divalent carbon numbers 2-12 which has the ester, amide, ether, or a hydroxyl group, or the ester, amide, and ether are expressed -- it is -- a polysulfide polymer, Reduction of the Mooney viscosity of a rubber compound is also expectable as indicated in the JP,61-4742, A gazette it not only can use as the rubber / a silica system binder of the rubber which has a double bond, and the system used as a silicate system bulking agent, but. It is equivalent to the performance of the wet grip nature required of rubbers, such as a tire, these days and low-fuel-consumption nature having high $\tan \delta$ of a low frequency region, and $\tan \delta$ of a high frequency region being low, and the silica system bulking agent which fills that military requirement is well used for this combination. Although bis(3-triethoxy silyl propyl)polysulfide is common as a binding material of this rubber and silica, the silanizing polysulfide polymer by this invention can raise the performance of rubber further as a binding material of silica/rubber.

[0030]

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to these.

[0031] [Example 1] Thiokol LP gas3 (made by Toray Industries thiokol incorporated company) of the molecular weight 1,000 was made to carry out mol addition of the ethyleneoxide 1.4 times to SH, and the end acquired the polysulfide polymer which is OH. It checked that made 3-isocyanatepropyl triethoxysilane of this mol react to the OH radical of this polymer under an amine catalyst, and IR infrared-absorption light of OH had disappeared. Next, it added and the powder sulfur which balances for setting the sulfur rank 2.0 of this silanizing polysulfide polymer to 4.0 was made to react under an amine catalyst. This polymer 40g and 10 g of bis(3-triethoxy silyl propyl)tetra sulfide were put into a 200-cc measuring flask, 0.5g of triethylamine supplied further, and decompression

deaeration was carried out at the same temperature for 30 minutes after mixing under the 80 **N₂ air current during 30 minutes. The bis(3-triethoxy silyl propyl)tetra sulfide in the obtained polymer checked that were decreasing to 4% after ending reaction, and the purpose polysulfide polymer was obtained, although just before place mixing measured with liquid chromatography was 14%. n of this substance is the about 3 number average molecular weight 1280.

Disulfide combination of the raw material polysulfide polymer turned into Tori, tetra, and penta combination by this substance by Raman analysis, and the average rank x was 4.

[0032][Example 2] -- a 300-cc measuring flask -- thiokol LP gas23 (SH2.9wt%) of the molecular weight 2200 The Toray Industries thiokol incorporated company make was 50 g, 18 g and 23.4g of bis(3-triethoxy silyl propyl)tetra sulfide were further made into the catalyst for powder sulfur, 0.2g of triethylamine was put in, and decompression deaeration was carried out at the same temperature for further 1 hour after mixing under 2-hour 80 **N₂ air current. Absorption of the place SH which measured the acquired output with IR infrared-absorption light had disappeared thoroughly, and its smell was also close to no odor. The viscosity in 25 ** of this output is 68 poise, and the purpose polysulfide polymer was obtained. the viscosity in 25 ** of this thing after putting this substance into a glass bottle and neglecting it for 90 ** and four days is 68 poise -- storage stability -- having excelled . n of this substance is the about 7 number average molecular weight 2100. Disulfide combination of the raw material polysulfide polymer turned into Tori, tetra, and penta combination by this substance by Raman analysis, and the average rank x was 4.

[0033][Example 3] -- a 300-cc measuring flask -- thiokol LP gas23 (SH2.9wt%) of the molecular weight 2200 The Toray Industries thiokol incorporated company make was 50 g, 18 g and 15g of gamma-mercapto propyltrimethoxysilane were further made into the catalyst for powder sulfur, 0.2g of triethylamine was put in, and decompression deaeration was carried out at the same temperature after mixing under 80 ** [per hour] N₂ air current for further 1 hour. Absorption of the place SH which measured the acquired output with IR infrared-absorption light had disappeared thoroughly, and its smell was also close to no odor. The viscosity in 25 ** of

this output is 90 poise, and the purpose polysulfide polymer was obtained. n of this substance is the about 9 number average molecular weight 2630. Disulfide combination of the raw material polysulfide polymer turned into Tori, tetra, and penta combination by this substance by Raman analysis, and the average rank x was 4.

[0034][Example 4] -- a 300-cc measuring flask -- thiokol LP gas23 (SH2.9wt%) of the molecular weight 2200 18 g and tetramethylthiuramdisulfide for 50 g and powder sulfur 4 g, [the Toray Industries thiokol incorporated company make] 23 g was further made into the catalyst for bis(3-triethoxy silyl propyl)tetra sulfide, 25g of toluene added triethylamine as 0.5 g and a solvent, and decompression deaeration was carried out at the same temperature for further 1 hour after mixing under 2-hour 80 **N2 air current. Absorption of the place SH which measured the acquired output with IR infrared-absorption light had disappeared thoroughly, and its smell was also close to no odor. The place which the viscosity in 25 ** of this output is 63 poise, and measured this output with liquid chromatography, It has checked that tetramethylthiuramdisulfide and bis(3-triethoxy silyl propyl)tetra sulfide which are the raw materials of this substance were decreasing in output, and the purpose polysulfide polymer was obtained. n of this substance is the about 5 number average molecular weight 1600. Disulfide combination of the raw material polysulfide polymer turned into Tori, tetra, and penta combination by this substance by Raman analysis, and the average rank x was 4.

[0035][Example 5] -- a 300-cc measuring flask -- thiokol LP gas23 (SH2.9wt%) of the molecular weight 2200 18 g and dibenzothiazyl disulfide for 50 g and powder sulfur 5 g, [the Toray Industries thiokol incorporated company make] 23 g was further made into the catalyst for bis(3-triethoxy silyl propyl)tetra sulfide, 25g of toluene added triethylamine as 0.3 g and a solvent, and decompression deaeration was carried out at the same temperature after mixing under 80 ** [per hour] N2 air current for further 0.5 hour. Absorption of the place SH which measured the acquired output with IR infrared-absorption light had disappeared thoroughly, and its smell was also close to no odor. The place which the viscosity in 25 ** of this output is 69 poise, and measured this output with liquid chromatography, It has checked that dibenzothiazyl disulfide and bis(3-triethoxy silyl propyl)

tetra sulfide which are the raw materials of this substance were decreasing in output, and the purpose polysulfide polymer was obtained. n of this substance is the about 5 number average molecular weight 1560. Disulfide combination of the raw material polysulfide polymer turned into Tetra, tetra, and penta combination by this substance by Raman analysis, and the average rank x was 4.

[0036][Example 6] -- a 300-cc measuring flask -- thiokol LP gas23 (SH2.9wt%.) of the molecular weight 2200 18 g and dithio dimorpholine for 50 g and powder sulfur 4 g, [the Toray Industries thiokol incorporated company make] 23 g was further made into the catalyst for bis(3-triethoxy silyl propyl)tetra sulfide, 24g of toluene added triethylamine as 0.4 g and a solvent, and decompression deaeration was carried out at the same temperature after mixing under 80 ** [per hour] N2 air current for further 0.5 hour. Absorption of the place SH which measured the acquired output with IR infrared-absorption light had disappeared thoroughly, and its smell was also close to no odor. The place which the viscosity in 25 ** of this output is 60 poise, and measured this output with liquid chromatography, It has checked that dithio dimorpholine and bis(3-triethoxy silyl propyl)tetra sulfide which are the raw materials of this substance were decreasing in output, and the purpose polysulfide polymer was obtained. n of this substance is the about 5 number average molecular weight 1600. Disulfide combination of the raw material polysulfide polymer turned into Tetra, tetra, and penta combination by this substance by Raman analysis, and the average rank x was 4.

[0037]
[Effect of the Invention]It becomes the binder with which the rubber/silica which six or less silanizing polysulfide polymer is not only excellent as a **** agent of rubber which has a double bond, but has a double bond exceeding 2 were excellent in the bonding number of sulfur in the repeating unit of this invention.

[Translation done.]